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INVESTIGATIONS ON THE PARAMAGNETIC RESONANCE IN COAL WITH A TRANSMISSION TYPE ELECTRON PARAMAGNETIC RESONANCE SPECTROMETER

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ABSTRACT. A simple transmission type electron paramagnetic resonance spectrograph operating at 3 2 cm wave length is briefly described. Preliminary investigations on the variation in the number of paramagnetic centres in coal samples with the temperature of carbonisation, are reported. The temperature variation results corroborate with those obtained by the British group of workers, but differ in certain respects from the observations of the Russian group. The samples from different depths in a mine have also been investigated, but they show a very small variation in the paramagnetic centre concentration.

INTRODUCTION

The electron paramagnetic resonance observed in coals has been studied recently by different groups of workers (Ingram *et al*, 1954; Ubersfeld, *et al*, 1954 and Garifyanov *et al*, 1957), but no conclusive theory of its origin has as yet been arrived at. Amongst the most interesting behaviours shown by coal are the variation in the absorption signal strength with carbonizing temperature (Ingram, Tapley and others, 1954), with the percentage of carbon present (Ingram, Tapley and others, 1954), and with the carbonization in presence and absence of Oxygen (Ingram and Tapley, 1955)

With a view to investigate and explain these phenomena we have studied the variations of the electron paramagnetic resonance signal strength with temperature of carbonization and also with the depths in a mine for naturally occurring coal samples. Section I of this paper describes briefly a simple transmission type spectrometer operating at 3 2 cm wave length. The results of the experiments are given in Section II and a discussion on them are incorporated in Section III.

SECTION I

THE ELECTRON PARAMAGNETIC RESONANCE SPECTROMETER

Figure 1 shows a block diagram of the Spectrometer. It employs a 723 A/B Klystron as the source of the microwave power. A resonant cylindrical

cavity in the TE_{11} mode having both input and output waveguide feeds is used. The transmitted power is detected by a crystal diode 1N23, housed in a tunable detector mount. The current to the electromagnet is supplied from a bank of

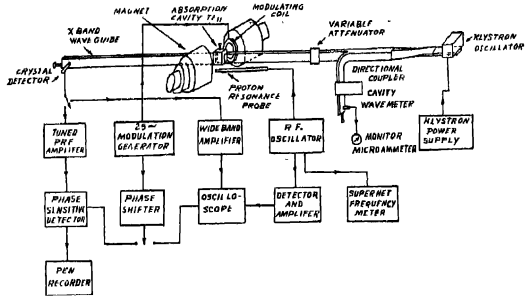

Fig. 1. Block diagram of the epr. Spectrometer.

batteries. With auxiliary sets of coils mounted on the pole piece, the steady field is modulated at 25 cps. The steady current is slowly varied over small ranges

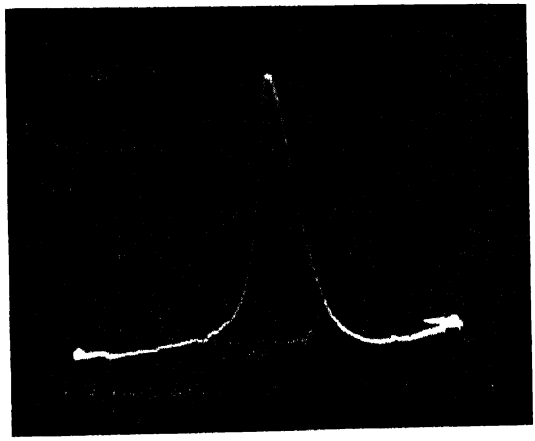

Fig. 2 Paramagnetic resonant absorption signal in lignite.

with a helipot coupled to a motor. For variation of the magnetic field over large ranges, a motor driven rheostat is used. The microwave frequency is measured by a Hewlett Packard Wavemeter, type X532A, coupled to the main wave guide

through a 10 db directional coupler. A proton resonance fluxmeter designed after Knoebel and Hahn (1951) is employed for the measurement of the steady magnetic field. With a superhet frequency meter, calibrated with reference to a primary frequency standard, type GR 1100-AP, the measurement of the magnetic field with an accuracy more than 1 part in 10^4 is very easily attained. Here the limitation to the accuracy in measuring the magnetic field is due to the inhomogeniety present in it. The present sensitivity of detection of the instrument is about 10μgm. of diphenyl picryl hydrazyl.

With the present arrangement signals having line widths upto 15 gauss can be observed on the oscilloscope screen. Derivatives of such and still broader lines can be recorded through phase-sensitive detector. Figures 2 and 3 show typical oscillogram and pen-recorder traces respectively for coal. In our experiments, the sharp absorption line of Diphenyl picryl hydrazyl is used as a standard of reference.

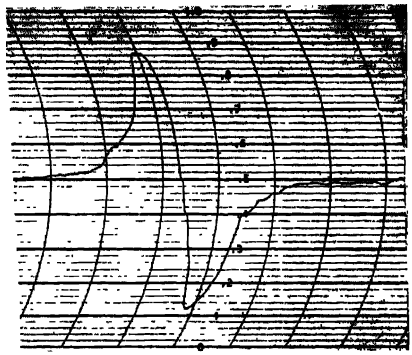

Fig 3 Derivative of the epr absorption signal in powdered lignite carbonised at 550°0.

SECTION II

INVESTIGATION ON COAL

A *Effect of the carbonizing temperature*

Briquetted samples of Lignite carbonized at different temperatures have been investigated. The temperature range runs from 250°C upto 750°C. Table 1 and figure 4 show the variation in the concentration of paramagnetic centres per gm of carbon as the carbonizing temperature is increased. No signal was observed for the sample carbonized at 750°C. A maximum in the concentration was shown for temperatures in between 550°C and 650°C. The line widths also increase with the increase in the temperature.

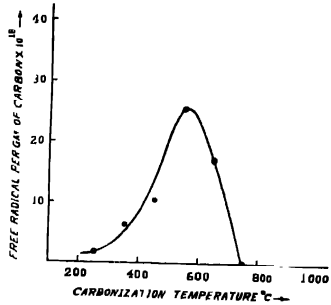

Fig 4. Variation of paramagnetic centre concentration with carbonizing temperature in briquetted lignite

Similar behaviour is shown by powdered Lignite treated to different temperatures (Table II). The paramagnetic centre concentration is greater in briquettes as compared to the corresponding powdered samples.

The total number of paramagnetic centres in the coal samples were determined from a comparison of the areas under the absorption signals for these samples with that for a known mass of diphenyl-picryl-hydrazyl, under identical setting of the spectrometer. For the line-width measurement full width at half maximum of diphenyl-picryl-hydrazyl signal was taken to be 3 gauss.

B. *Effect of depth* :

To study the effect of depth on the concentration of paramagnetic centres produced, we have investigated samples obtained from different depths of a mine. Depths ranging from 760 ft. up to 2876 ft. have been covered. The line width and also the concentration of paramagnetic centres per gm of carbon for these samples are given in Table III.

TABLE I

Line width and paramagnetic center concentration in briquetted lignites carbonized at different temperatures

Temperature	Line width in gauss	No. of paramagnetic centres per gm. of carbon
Not heated	3.4	1.0×10^{18}
250°C	4.2	1.5×10^{18}
350°C	4.4	6.4×10^{18}
450°C	4.7	10.4×10^{18}
550°C	4.8	25.8×10^{18}
650°C	6.3	17.4×10^{18}
750°C	×	×

TABLE II

Line width and paramagnetic centre concentration in powdered lignites carbonized at different temperatures

Temperature	Line width in gauss	No. of paramagnetic centres per gm of carbon
250°C	3 8	2.2×10^{18}
350°C	3 8	$2\ 2\times10^{18}$
450°C	4 2	8.7×10^{18}
550°C	4 6	$10\ 3\times10^{18}$
650°C	5 5	10.1×10^{18}
750°C	×	×

TABLE III

Line width and paramagnetic centre concentration in coal samples from different depths of a mine

Depth from the surface	Line width in gauss	No. of paramagnetic centres per gm. of carbon
760′–7″ to 765′ 0″	4.7	$1\ 9\times10^{19}$
1589′–7″ to 1599′–5″	5 0	$2\ 0\times10^{19}$
1944′ 6″ to 1951′ 0″	4 9	2.2×10^{19}
2521′ 6″ to 2526′ 10″	4 9	2.4×10^{19}
2866′ 0″ to 2876′–0″	4 9	$2\ 0\times10^{19}$

SECTION III

DISCUSSION

Our results show that the concentration of paramagnetic centres increases steadily up to a carbonizing temperature of 550°C. This is in absolute agreement with the observations of the British group of workers (Ingram *et al*, 1954) and also with those of the Russian workers (Garifyanov *et, al*, 1957). We find, for the maximum absorption at 550°C, for the powdered lignite, the number of paramagnetic centres per gm of carbon is 1.0×10^{19} and for briquettes it is 2.6×10^{19}, while from Ingram's (1954) report this figure comes out to be about 6×10^{19}. We assign the difference in the numerical values to be due to different types of specimens used in the experiments. However, our results cannot be compared quantitatively with those of the Russian group, for their data are given in relative terms.

There is, however, an important difference between our observations and those of the Russians. They observe that if the thermally treated samples are subjected to weathering in air, quite strong signals are observed for the samples heated to 750°C and to 900°C, while studies immediately after the heat treatment show no signal for those temperatures. But, in our case, all the samples after being carbonised at high temperatures were subjected to normal atmospheric condition for more than two months and no signal was observed for the sample treated up to 750°C. Also this behaviour observed by the Russians is found only in powdered samples and not in briquettes.

The data in Table 3 indicate only a very small variation of the paramagnetic centre concentration with depth. The line width is nearly constant. Ingram, Tapley and others (1954) observed large variation of signal strength with carbon percentages for samples having more than 80% carbon content, while for lower concentrations (as in our case) the absorption signal is expected to be nearly independent of carbon percentage. So the observed small variation in the signal cannot be attributed to the change in carbon percentage, specially since we are concerned only over a small range of its variation.

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